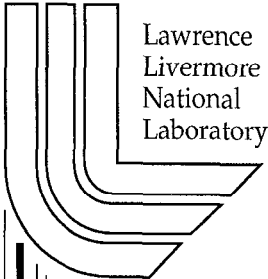


Results of Plug-Flow Reactor Experiments with Crushed Tuff at 280°C and 300°C

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September 2, 1999

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Results of Plug-Flow Reactor Experiments with Crushed Tuff at 280°C and 300°C

by

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Abstract

We report on the results to date for two plug-flow reactor experiments, PFR-11 and PFR-13, designed to simulate reactive transport chemical and physical processes. These experiments provide a physical model of idealized one-dimensional plug flow and chemical reaction using deionized water and crushed Topopah Springs Tuff (Tsw2). Data consist of effluent ion concentrations and pH measurements taken at several times during both experiments and limited mineralogical analysis of post-test solid phases for PFR-11.

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Introduction

Changes in mineralogy, mineral chemistry and water chemistry that may occur at Yucca Mountain in response to the potential emplacement of high-level radioactive waste will be a complex function of many factors, including the initial mineralogy and water chemistry, and the thermal-hydrological environment. To gain confidence in our ability to model water-rock interactions that may occur this system, we need to validate our models with well-constrained and well-documented laboratory experiments.

The plug-flow reactor (PFR) experiments reported here provide a physical model of idealized one-dimensional plug flow. These experiments consist of flowing deionized water through a narrow column of porous material. In order to accelerate the geochemical reactions that might occur in this system, many of which occur very slowly at temperature below 100°C, we conduct them at temperatures above 100°C and at pressures above 1 atm so that the system remains saturated.

The plug material used in these experiments is from Topopah Spring Tuff. An earlier experiment with this material (PFR-5, see Johnson et al., 1998), indicated the possible formation of secondary minerals, but the complete characterization of these volumetrically-minor phases was difficult. For the current two experiments, a higher temperature and flow rate was chosen in an attempt to encourage the formation of these secondary minerals.

These plug flow reactor experiments also differ from previous experiments in that we have improved our post-test sampling technique for the solid material. In prior experiments, the post-test sampling of the tuff was performed by using a push rod to force the tuff through the core. This method only allowed for rough estimates of the actual sample position along the core, and introduced the possibility of the intermixing of tuff along the length of the core during post-test recovery of the tuff. In our current experimental design, a gold liner was inserted into the column prior to the addition of the tuff. This liner could then be removed intact at the completion of the experiment, allowing for the sampling of the tuff without intermixing the crushed rock along the flow path. This allows for the better spatial characterization of the mineralogical changes occurring in the crushed rock.

This is a status report on these experiments, PFR-11 and PFR-13, which differ only in temperature. PFR-11 was conducted at 280°C and PFR-13 was conducted at 300°C. Data obtained to date consist of effluent ion concentrations and pH measurements taken at several times during the experiments for both PFR-11 and PFR-13 and limited mineralogical analysis of post-test solid phases for PFR-11. Post-test solid samples are available for further analyses in the future. No analysis or modeling is included in this report.

Experimental design

Sample characterization and preparation

The plug material selected is a sample from the Topopah Spring Member of the Paintbrush Tuff (Tsw2), Yucca Mountain, NV. The Tsw2 is a densely welded, completely devitrified ashflow tuff of nominally high-silica rhyolite composition. This phenocryst-poor (< 2%) tuff consists largely (~ 99 vol.%) of the former glassy matrix now devitrified to fine crystals of cristobalite, alkali feldspar, and quartz. Knauss and Wolery (1986) and Knauss et al. (1985) provide detailed compositional data for both whole rock and individual mineral analyses performed on this material.

The Tsw2 has several desirable features: relatively simple, well-characterized mineralogy which includes only trace phases that contain redox elements (Delany, 1985; Knauss and Wolery, 1986, Knauss et al., 1985); thermodynamic data at elevated temperature are available for all of the relevant minerals and aqueous solutes; and specific-surface areas and kinetic data at elevated temperatures exist for all the major primary and many potential secondary minerals.

In the present study, coarse grains were prepared by carefully crushing the tuff using a flat plate grinder with tungsten carbide plates. These grains were sieved to a nominal size of $100 \pm 25 \mu\text{m}$ and then cleaned repeatedly in isopropanol using an ultrasonic bath and gravitational settling techniques. Scanning Electron Microscopy (SEM) examination confirmed that this washing method removed the bulk of fine particles from coarse grain surfaces. SEM analysis revealed that the $100 \mu\text{m}$ grains are composed of myriad individual cristobalite, alkali feldspar, and quartz crystals of 3–10 μm size fraction (Johnson, 1998).

Description of plug-flow reactor

A commercial, high-temperature plug-flow reactor was modified for these experiments. The reactor consists of a pure Ti-column (30-cm length; 0.66-cm diameter) and associated three-zone furnace, a controller, high-pressure pulseless two-piston metering flow pump, transducers upstream and downstream from the column, and a gas-balanced, dome-type back pressure regulator. All fluid-wetted components are composed of titanium, inconel, stellite, viton, or teflon. This reactor operates at temperatures up to 350°C and pressures up to 300 bar. The fluid pump can achieve flow rates of 0.0002 to 10 ml per minute at pressures up to 5,000 psi (345 bar).

The crushed 75–125 μm grains were loose-packed to fill the column, resulting in an initial porosity of approx. 40-45%. In each run, steady-state fluid infiltration rates and elevated temperature-pressure conditions were achieved within approximately one hour. Isothermal conditions were maintained by using rheostats to control the applied voltage to each of three heaters positioned along the column. Table 1 lists the physical parameters of experiments PFR-5 (Johnson et al., 1998), PFR-11 and PFR-13.

Sampling and analysis

Fluid chemistry

Samples of the fluid exiting the column were collected on a periodic basis in both PFR-11 and PFR-13. In all cases, the fluid was collected into a plastic syringe through a Luer-type connector. Aqueous samples for cation, anion and pH analyses were collected in plastic syringes.

The fluid for cation analysis (~3 ml) was collected in a syringe that had been preloaded with 2 ml 0.08 molal NH_4OH . The combined fluid was filtered through a 0.45 μm syringe filter into a plastic sample tube. The cation (Al, Ca, Fe, K, Mg, Na and Si) concentrations were determined using inductively-coupled plasma emission spectrometry (ICP).

For all anion analyses, sample fluid was filtered through a 0.45 μm syringe filter. The anions Br, Cl, F, NO_2 , NO_3 , PO_4 and SO_4 were determined using ion chromatography (IC). The carbonate anions were determined as total CO_2 using an infrared CO_2 analyzer and reported as HCO_3^- .

The solution pH was determined using the NBS standard (Bates, 1964). The sample was filtered through a 0.45 μm syringe filter and allowed to cool to room temperature before analysis.

Mineralogical

Mineralogical analysis was performed for PFR-11 only. At the end of the experiment, the gold liner was pinched at both ends and removed from the column. The total length was cut into 29 separate, approximately 1 cm samples that were numbered according to their position along the length of the reactor.

X-ray diffraction (XRD) analyses were performed on a subset of six of these samples at points at the beginning, middle, and end of the plug flow reactor length. The samples analyzed were, from the beginning (2 and 4), middle (14 and 16), and end (27 and 29). A portion of unreacted material (called sample 0) was also analyzed and used to assess reaction progress with length.

Results

Fluid chemistry

The fluid chemistry results from PFR-11 and PFR-13 experiments are shown in Tables 2-7.

Mineralogical

Mineral abundance of quartz and cristobalite determined in the samples by XRD are summarized in Table 8.

The XRD results for feldspar in all the reacted samples were similar to those in the sample of unreacted tuff. No definitive peaks for secondary phases were evident. To identify the presence of secondary phases, additional analytical work would be necessary.

Discussion, Modeling and Conclusions

Preliminary data analysis and reactive transport modeling of the results has been performed, but the project was terminated before this work could be completed.

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Table 1. Summary of PFR experiments with Tsw2 and deionized water

	PFR-5*	PFR-11	PFR-13
Temperature, °C	240	298	281
Pressure, bar	84	140	152
Plug length, cm	26.3	29.7	29.7
Plug diameter, cm	0.66	0.58	0.58
Flow rate, ml/day	25.0	150	150
Duration, days	36.0	9.3	14.0

*Reported in Johnson et al., 1998

Table 2. Cation water chemistry (PFR-11)

Elapsed Time days	Al ³⁺ mg/kg	Ca ²⁺ mg/kg	Fe ²⁺ mg/kg	K ⁺ mg/kg	Mg ²⁺ mg/kg	Na ⁺ mg/kg	Si ⁴⁺ mg/kg
0.00	<0.09	0.20	<0.03	<0.8	0.03	1.7	<0.9
0.07	6.54	0.48	0.24	13.4	0.03	8.1	364
0.18	11.9	0.46	0.61	10.6	0.03	14.2	492
0.3	7.37	0.33	0.22	3.9	0.03	12.6	441
1.0	7.74	0.36	0.35	3.6	<0.02	10.4	454
1.3	7.77	0.34	0.26	3.3	<0.02	11.0	464
4.1	6.54	0.21	0.03	2.8	0.03	10.7	460
5.2	7.35	0.31	0.16	2.8	0.03	12.1	469
6.0	7.28	0.35	0.05	2.7	0.03	12.6	487
6.3	6.89	0.22	0.05	2.2	0.03	11.9	467
7.0	7.00	0.20	0.02	1.5	0.03	12.9	471
8.0	7.40	0.21	0.03	2.1	0.03	13.3	459
9.3	2.69	0.27	0.02	2.2	0.03	16.6	539

Table 3. Anion water chemistry (PFR-11)

Elapsed Time days	Br ⁻ mg/kg	Cl ⁻ mg/kg	F ⁻ mg/kg	HCO ₃ ⁻ mg/kg	NO ₂ ⁻ mg/kg	NO ₃ ⁻ mg/kg	PO ₄ ³⁻ mg/kg	SO ₄ ²⁻ mg/kg
0.00	<0.1	0.43	<0.05	<2.5	<0.1	<0.1	<0.1	0.64
0.07	<0.1	0.60	0.54	•	<0.1	<0.1	0.14	0.93
0.18	<0.1	1.81	3.73	•	<0.1	<0.1	0.11	1.16
0.3	<0.1	0.78	1.59	•	<0.1	<0.1	<0.1	0.78
1.0	<0.1	0.58	0.79	•	<0.1	<0.1	<0.1	0.52
1.3	<0.1	0.66	0.46	•	<0.1	0.10	<0.1	0.68
4.1	<0.1	0.50	0.23	<3.3	<0.1	<0.1	<0.1	0.36
5.2	<0.1	0.84	0.35	•	<0.1	0.13	<0.1	0.79
6.0	<0.1	0.54	0.22	•	<0.1	<0.1	<0.1	0.39
7.0	<0.1	0.63	0.28	•	<0.1	<0.1	<0.1	0.52
8.0	<0.1	0.48	0.25	•	<0.1	<0.1	<0.1	0.51
9.3	<0.1	0.56	0.38	•	<0.1	<0.1	<0.1	0.77

Table 4. pH evolution (PFR-11)

Elapsed Time days	pH
0.00	7.89
0.07	7.52
0.18	6.69
0.3	7.24
1.0	7.18
1.3	7.66
4.1	7.49
5.2	7.60
6.0	7.83
7.0	7.59
8.0	7.93
9.3	7.78

Table 5. Cation water chemistry (PFR-13)

Elapsed Time days	Al ³⁺ mg/kg	Ca ²⁺ mg/kg	Fe ²⁺ mg/kg	K ⁺ mg/kg	Mg ²⁺ mg/kg	Na ⁺ mg/kg	Si ⁴⁺ mg/kg
0.00	0.22	0.30	<0.03	<0.8	<0.02	<0.2	0.18
0.05	<1.0	0.45	<0.03	<0.8	<0.02	<0.2	43.0
0.10	3.16	0.30	0.03	3.0	<0.02	6.4	244
0.15	4.70	0.13	<0.03	3.9	<0.02	11.0	425
0.20	5.35	0.24	<0.03	4.8	<0.02	11.7	481
0.24	6.10	0.12	<0.03	3.6	<0.02	10.5	513
0.95	7.85	0.10	0.05	2.7	<0.02	12.6	483
2.0	7.99	0.07	0.03	1.5	<0.02	11.7	484
2.9	8.07	0.10	0.05	1.5	<0.02	12.0	485
5.1	7.78	0.06	0.06	1.7	<0.02	12.9	480
6.9	8.14	0.10	0.07	1.8	<0.02	13.2	467
7.9	8.46	0.05	0.07	1.0	<0.02	13.4	460
9.0	10.09	0.10	0.15	1.5	<0.02	15.2	461
9.9	8.96	0.07	0.07	1.8	<0.02	14.1	461
11.9	9.52	0.10	0.07	0.8	<0.02	14.8	467
12.9	9.50	0.07	0.03	<0.8	<0.02	15.6	471
14.0	10.25	0.07	<0.03	<0.8	<0.02	16.2	465

Table 6. Anion water chemistry (PFR-13)

Elapsed Time days	Br ⁻ mg/kg	Cl ⁻ mg/kg	F ⁻ mg/kg	HCO ₃ ⁻ mg/kg	NO ₂ ⁻ mg/kg	NO ₃ ⁻ mg/kg	PO ₄ ³⁻ mg/kg	SO ₄ ²⁻ mg/kg
0.00	<0.2	0.23	<0.1	<3.6	<0.2	<0.2	<0.2	0.88
0.05	<0.2	0.34	0.27	•	<0.2	<0.2	<0.2	0.85
0.10	<0.2	0.71	0.52	•	<0.2	<0.2	<0.2	1.1
0.15	<0.2	0.74	1.1	•	<0.2	<0.2	<0.2	1.2
0.20	<0.2	1.0	1.2	•	<0.2	<0.2	<0.2	1.1
0.24	<0.2	1.5	1.6	•	<0.2	0.26	<0.2	1.8
0.95	<0.2	0.65	0.34	•	<0.2	<0.2	<0.2	0.78
2.0	<0.2	1.0	0.47	•	<0.2	0.26	<0.2	1.1
2.9	<0.2	1.1	0.33	•	<0.2	0.26	<0.2	1.5
5.1	<0.2	0.60	0.27	•	<0.2	<0.2	<0.2	0.86
6.9	<0.2	0.48	0.32	•	<0.2	0.30	<0.2	1.2
7.9	<0.2	0.61	0.28	•	<0.2	1.4	<0.2	0.93
9.0	<0.2	0.73	0.18	<3.6	<0.2	1.9	<0.2	1.5
9.9	<0.2	0.38	0.22	•	<0.2	0.52	<0.2	0.58
11.9	<0.2	0.90	0.28	•	<0.2	3.0	<0.2	1.3
12.9	<0.2	0.47	0.20	•	<0.2	<0.2	<0.2	1.0
14.0	<0.2	1.0	0.13	•	<0.2	<0.2	<0.2	0.93

Table 7. pH evolution (PFR-13)

Elapsed Time days	pH
0.00	6.03
0.05	7.28
0.10	6.68
0.15	6.97
0.20	7.30
0.24	7.39
0.95	7.61
2.0	7.53
2.9	7.57
5.1	7.68
6.9	7.98
7.9	7.92
9.0	7.98
9.9	7.96
11.9	7.99
12.9	7.97
14.0	8.02

Table 8. Quartz and cristobalite analysis (PFR-11)

Sample identifier	Quartz (% by weight	Cristobalite (% by weight
0	24.6	16.4
2	0.4	1.6
4	0.6	2.7
14	18.6	5.3
16	16.5	14.0
27	26.4	33.0
29	17.1	10.0